

PATENT ABSTRACTS OF JAPAN

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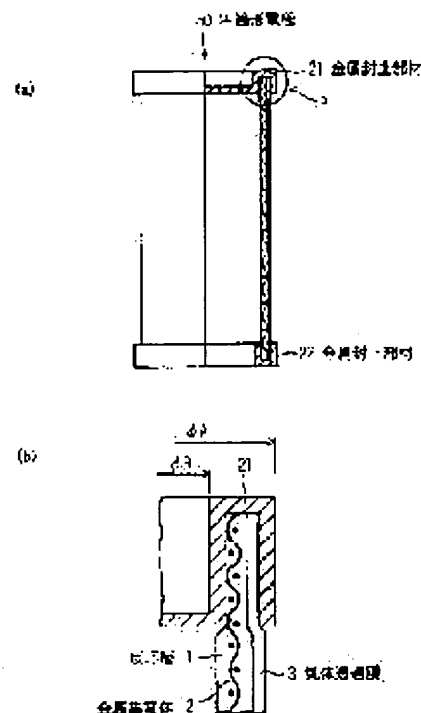
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(54) CYLINDRICAL ELECTRODE AND AIR ZINC BATTERY USING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cylindrical air zinc battery that comprises a cylindrical electrode excellent in mechanical strength, has an excellent electrolyte leakage-resistant property and discharging characteristic, has high discharging capacity and also has small dispersion of current collection.

SOLUTION: A cylindrical electrode 50 is composed of: a disc-like metal sealing member 21 having a cylindrical hollow electrode comprised of a reaction layer 1 having oxidation-reduction capability, a metal collector 2 and a water repellent gas passing film 3 and an annular groove; and an annular metal sealing 22 having an annular groove; and is formed by inserting one open end of the electrode into the groove of the disc-like metal sealing member 21 and crimping it, and inserting the other open end of the electrode into the groove of the annular metal sealing member 22 and crimping it. A cylindrical air zinc battery is structured by using the cylindrical electrode 50.



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(54) [Title of the Invention] CYLINDRICAL ELECTRODE AND AIR - ZINC BATTERY
USING SUCH ELECTRODE

(57) [Abstract]

[Object] The object of the present invention is to provide a cylindrical electrode having excellent mechanical strength and a cylindrical air - zinc battery having excellent resistance to leakage and discharge characteristic and also a high discharge capacity and small spread in current collection.

[Means to Attain the Object] A cylindrical electrode 50 comprising a hollow tubular electrode consisting of a reaction layer 1 having an oxygen reduction capability, a metallic collector 2, and a water-repellent gas permeable membrane 3, a ring-like metallic sealing member 22 having a ring-like groove, and a disk-like metallic sealing member 21 having a ring-like groove, wherein one open end of the electrode is inserted into the groove in the ring-like metallic sealing member 22 and attached thereto by pressure, and another open end of the electrode is inserted into the groove in the disk-like metallic sealing member 21 and attached thereto by pressure. A cylindrical air - zinc battery fabricated by using the cylindrical electrode 50.

[Patent Claims]

[Claim 1] A cylindrical electrode comprising:
a hollow tubular electrode consisting of a reaction layer having an oxygen reduction capability, a metallic collector, and a water-repellent gas permeable membrane,
a ring-like metallic sealing member having a ring-like groove, and
a disk-like metallic sealing member having a ring-like groove, wherein

one open end of said electrode is inserted into the groove in said ring-like metallic sealing member and attached thereto by pressure, and another open end of said electrode is inserted into the groove in said disk-like metallic sealing member and attached thereto by pressure.

[Claim 2] The cylindrical electrode as described in Claim 1, wherein the central portion of the disk in said disk-like metallic sealing member protrudes to the outside from the cylindrical portion of the electrode.

[Claim 3] The cylindrical electrode as described in Claim 1, wherein the depth of the groove in said ring-like metallic sealing member and the depth of the groove in said disk-like metallic sealing member is no less than 2.5% and no more than 20% of the length of the cylindrical portion of the electrode.

[Claim 4] The cylindrical electrode as described in Claim 1, wherein said ring-like metallic sealing member and said disk-like metallic sealing member are formed from metallic sheets.

[Claim 5] The cylindrical electrode as described in Claim 1, wherein the outer walls of the grooves in said ring-like metallic sealing member and said disk-like metallic sealing member are subjected to ring-like projection processing after the insertion of the electrode open ends.

[Claim 6] An air - zinc battery in which the side of the cylindrical electrode described in Claim 1 which is sealed with the disk-like metallic sealing member is inserted toward the bottom of an open-end cylindrical positive electrode case also serving as a positive electrode terminal and brought into intimate contact therewith to provide for current collection on the positive electrode side.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a cylindrical electrode having excellent discharge characteristic and resistance to leakage.

[0002]

[Prior Art Technology] Recent progress attained in the field of portable electronic devices has been creating an ever growing demand for batteries, which are power sources for the devices, that can produce a higher electric current and can be used for a longer time. More recently, great attention has been focused on environmental protection and effective utilization of natural resources, and a strong social demand was produced for technology satisfying such requirements.

[0003] Fuel cells and air - zinc batteries using oxygen as a positive electrode active material have been known as effective battery systems meeting the above-described demands. Such battery systems produce smaller effect on environment than other battery systems because the positive electrode active material is oxygen. Moreover, they are superior to other battery systems in terms of the produced electric capacity. Air - zinc batteries have an especially excellent

energy density per unit volume and are expected to become batteries of choice for future portable devices.

[0004] Small button- or coin-like air – zinc batteries are currently mainly used as power sources for hearing aids, pagers and the like. However, since such small batteries have limited application, there is a demand for cylindrical air – zinc batteries which are suitable for wider applications.

[0005] The air – zinc batteries use oxygen as a positive electrode active material, zinc as a negative electrode active material, and a strongly alkaline aqueous solution as an electrolytic solution. Therefore, sufficient measures against leakage of electrolytic solution have to be taken in the batteries of this type.

[0006] A cylindrical air – zinc battery that has been suggested earlier will be explained below with reference to Fig 6 and Fig 7. Fig 6 shows the structure of the cylindrical electrode that has been suggested earlier. Fig 6(a) is its partial cross section, Fig 6(b) is the exploded view of the portion indicated as P₂ in Fig 6(a). Fig 7 shows the structure of the cylindrical air – zinc battery that has been suggested earlier.

[0007] The conventional cylindrical electrode 60, as shown in Fig 6(a), is a hollow tubular electrode which, as shown in Fig 6(b) comprises a reaction layer 1 having an oxygen reduction capability, a metallic collector 2, and a water-repellent gas-permeable membrane 3.

[0008] In the structure of the air – zinc battery 61 using the cylindrical electrode 60, as shown in Fig 7, the cylindrical electrode 60 serves as a positive electrode, and the open end on the positive electrode terminal side of the cylindrical electrode 60 is arranged in the prescribed positions of the gasket 10, positive electrode terminal sheet 14, and gasket 11. Furthermore, the metallic collector 2 and the positive electrode terminal sheet 14 are electrically connected to each other via a lead wire 9. Furthermore, an air diffusion layer 4 is provided on the outer side of the gas permeable membrane 3, and an open-end tubular separator 5 consisting of a nonwoven fabric or the like is attached to the inner wall of the reaction layer 1 so that its bottom portion is on the positive electrode terminal sheet 14 side. A gelled negative electrode mix 6 consisting of powdered zinc, aqueous solution of potassium hydroxide, and a thickening agent is placed inside the separator 5.

[0009] Furthermore, a gasket 8 is installed in the prescribed position in the opening of the cylindrical electrode 60 at the negative electrode terminal side, then a negative electrode terminal sheet 13 is installed, an outer case 12 having an air opening 16 is placed and the structural components located inside the battery are sealed by inwardly bending the open portion of the outer case 12 and the neck portion 15 obtained by drawing. The collection of current at the negative electrode is conducted by electrically connecting a negative electrode terminal sheet 13 and a nail-like negative electrode collector pin 7 inserted into the negative electrode mix 6. Furthermore, until the air battery is used, the air opening 16 has to be closed; a sealing member used for this purpose is not shown in the figure.

[0015] In accordance with the invention disclosed in Claim 2, the central portion of the disk in the disk-like metallic sealing member protrudes to the outside from the cylindrical portion of the electrode.

[0016] In accordance with the invention disclosed in Claim 3, the depth of the groove in the ring-like metallic sealing member and the depth of the groove in the disk-like metallic sealing member is no less than 2.5% and no more than 20% of the length of the cylindrical portion of the electrode.

[0017] Furthermore, in accordance with the invention disclosed in Claim 4, the ring-like metallic sealing member and the disk-like metallic sealing member are formed from metallic sheets.

[0018] In accordance with the invention disclosed in Claim 5, the outer walls of the grooves in the ring-like metallic sealing member and the disk-like metallic sealing member are subjected to ring-like projection processing after the insertion of the electrode open ends.

[0019] In accordance with the invention disclosed in Claim 6, a cylindrical air – zinc battery is provided in which the side of the cylindrical electrode described in any claim from Claim 1 to Claim 5, which is sealed with the disk-like metallic sealing member, is inserted toward the bottom of an open-end cylindrical positive electrode case also serving as a positive electrode terminal and brought into intimate contact therewith to provide for current collection on the positive electrode side.

[0020] In accordance with the invention described in Claim 1, both open ends of the cylindrical electrode are rigidly secured with a ring-like metallic sealing member and a disk-like metallic sealing member having a structure such that they clamp the open ends. Therefore, the metallic collector and the metallic sealing member are brought into intimate contact, a stable electric connection is obtained, the spread in current collection is decreased, and the reaction layer is compressed together with the gas permeable membrane. As a result, the mechanical strength of the electrode is increased and no deformation is generated even when an external stress is applied. Therefore, tightly sealed state of electrolytic solution is guaranteed and resistance to leakage is improved.

[0021] Furthermore, in accordance with the invention described in Claim 2, the central portion of the disk-like metallic sealing member protrudes to the outside of the cylindrical electrode. As a result, the discharge capacity can be increased.

[0022] Moreover, in accordance with the invention described in Claim 3, the depth of grooves for insertion of the open portions of the cylindrical electrode, which are provided in the disk-like metallic sealing member and the ring-like metallic sealing member, is optimized, which makes it possible to improve additionally the leakage resistance and increase the discharge capacity.

[0023] Furthermore, in accordance with the invention described in Claim 4, the ring-like metallic sealing member and the disk-like metallic sealing member are formed from metallic sheets by drawing. Therefore, they can be manufactured with high productivity at a low cost.

[0024] Moreover, in accordance with the invention disclosed in Claim 5, the outer walls of the grooves in the ring-like metallic sealing member and the disk-like metallic sealing member are subjected to ring-like projection processing after the insertion of the electrode open ends. Therefore, the leakage resistance and current collection characteristic are additionally improved.

[0025] Furthermore, in accordance with the invention disclosed in Claim 6, a cylindrical air - zinc battery can be provided in which the internal resistance and spread in the resistance can be reduced and which has excellent discharge characteristic and resistance to leakage.

[0026]

[Preferred Embodiment of the Present Invention] The preferred embodiment of the present invention will be described below with reference to Figs 1 to 5. Fig 1 illustrates an embodiment of the cylindrical electrode in accordance with the present invention. Fig (a) is a partial cross section thereof, Fig (b) is an exploded view of the portion indicated with a reference symbol P₁ in Fig 1. Figs 3 to 5 illustrate other embodiments of the cylindrical electrode in accordance with the present invention.

[0027] Embodiment 1

A cylindrical electrode will be described below with reference to Fig 1. The electrode was fabricated in the following manner. Manganese oxide as a catalyst having a redox capability, carbon black, and an aqueous dispersion of polytetrafluoroethylene having a content of solids of 60% were mixed so as to obtain a ratio of solids of 20 : 50 : 30 and to provide a paste-like reaction layer mixture. This reaction layer mixture was coated on a metal collector 2 made of a cylindrical stainless steel net plated with nickel. Subsequent drying and press rolling produced a cylindrical reaction layer 1 having a thickness of 0.8 mm. The reaction layer 1 was then inserted in a cylindrical gas permeable membrane 3 having a thickness of 0.1 mm and a water repellent function. Subsequent press rolling tightly bonded the gas permeable membrane 3 to the reaction layer 1 and produced a cylindrical electrode.

[0028] Then, metallic sealing members 21, 22 were fit onto both open ends of the cylindrical electrode fabricated in the above-described manner so that the open ends were inserted in the grooves provided on the metallic sealing members, and the metallic sealing members were compressed in the radial direction along the whole periphery to obtain a cylindrical electrode 50. In this process, the metallic sealing members 21, 22 were attached under pressure to the metallic collector 2 at the open end portions, thereby providing for electric connection between them. At the same time, the reaction layer 1 and the gas permeable membrane 3 were also compressed in the radial direction and their strength was increased. In the above-described embodiment, the metallic sealing member 21 had a disk-like shape, and the metallic sealing member 22 had a ring-like shape.

[0029] Means employed for the above-mentioned compression can be a method reducing an outer diameter A shown in Fig 1(b), a method enlarging the inner diameter B, or a combination of these two methods. Copper, brass, and steel or stainless steel plated with nickel can be used

for the metallic sealing members 21, 22. When copper or brass is used, it is preferred that it be plated with tin.

[0030] The structure of an air – zinc battery 51 employing the cylindrical electrode 50 fabricated in the above-described manner is shown in Fig 2. An air diffusion layer 4 consisting of a nonwoven fabric or the like was installed outside of the air permeable membrane 3 of the cylindrical electrode 50, and the resulting assembly was inserted in a positive electrode case 23 also serving as a positive electrode terminal. The positive electrode case 23 also serving as a positive electrode terminal had an air inlet opening 16 in its side surface. Then, an open-end cylindrical separator 5 consisting of nonwoven fabric made of a natural pulp material was inserted, so as to be in close contact with the reaction layer 1, from an open portion on the side of the ring-like metallic sealing member 22 along the inner surface of the cylindrical electrode 50. Then, the space inside the separator 5 was filled with a gelled negative electrode mix 6 consisting of powdered zinc, an aqueous solution of potassium hydroxide, and a thickening agent.

[0031] The gasket 8 was then inserted in the open portion of the positive electrode case 23. The gasket 8 was used to prevent the contact between the negative electrode mix 6 and the inner side of the metallic sealing member 22. This is necessary because if the powdered zinc present in the negative electrode mix 6 contacts with the metallic sealing member 22, a local cell is formed and the discharge capacity of zinc serving as a negative electrode active material is decreased. Furthermore, a nail-like negative electrode collector pin 7 is inserted in through the center of the gasket 8 to reach the negative electrode mix 6.

[0032] The open portion of the positive electrode case 23 is then mechanically bent inward and sealed by caulking. As a result, a cylindrical air – zinc battery 51 is obtained which has an outer diameter of 14 mm and a height of 50 mm. In such a battery, current collection at the cylindrical electrode 50 and the positive electrode case 23 also serving as a positive electrode terminal is guaranteed because the metallic sealing members 21, 22 fit onto the cylindrical electrode 50 are strongly attached under pressure to the inner surface of the positive electrode case 23. In other words, the metallic collector 2 of the cylindrical electrode 50 is connected to the positive electrode case 23 via metallic sealing members 21, 22 at a low contact resistance. Current collection at the negative electrode is guaranteed by the fact that the nail-like negative electrode collector pin 7 was inserted in the center of the gasket 8, passed through the gasket 8, and reached the negative electrode mix 6, his other end being connected to the negative electrode terminal plate 13.

[0033] The air – zinc battery 51 fabricated in the above-described manner and the air – zinc battery 61 as the conventional example were fabricated so as to have the same size, and the following characteristics of the batteries were measured.

(1) Discharge capacity : a discharge capacity at a load of 10 Ohm and an end voltage of 0.9 V was measured.

(2) Leakage : the batteries were discharged at a load of 10 Ohm and an end voltage of 0.9 V and the occurrence of leakage after 100 h was determined.

The results obtained are shown in Table 1.

[0034]

[Table 1]

Total number of batteries used for measurements : 20

	Discharge capacity via 10 Ohm load (mAh)	Occurrence of leakage after 100 h (number of batteries; the discharge end voltage is 0.9 V)
Embodiment 1	2425	0
Embodiment 2	2558	0
Conventional example	1962	11

[0035] As shown in Table 1, the discharge capacity of the air – zinc battery 51 of Embodiment 1 was higher than that of the air – zinc battery 61 having the conventional structure. Furthermore, no leakage after discharge was observed in the batteries of the embodiment.

[0036] Embodiment 2

An air – zinc battery 51 was fabricated in the same manner as in Embodiment 1, except that the central portion of the dick-like metallic sealing member 21 protruded to the outside beyond the cylindrical portion of the electrode, as shown in Fig 3. Measurements were conducted in the same manner as described above. The measurement results are presented in Table 1. It is preferred that the length C between the electrode clamping portion of the metallic sealing member 22 and the protruding portion of the metallic sealing member 21 shown in Fig 1 exceeded the length D between the electrode clamping portions of the metallic sealing member 21, 22.

[0037] As shown in Table 1, the discharge capacity of the air – zinc battery 51 of Embodiment 2 was higher than that obtained in Embodiment 1. Furthermore, no leakage after discharge was observed in the batteries of the Embodiment 2.

[0038] Embodiment 3

An air – zinc battery 51 was fabricated in the same manner as in Embodiment 51, except that the respective depths E_1 , E_2 of the grooves in the metallic sealing members 21, 22 fitted onto the peripheral portion of the electrode were varied within a range of 1.0-30% of the electrode length F (in this case, $E_1 = E_2$) and that the central portion of the metallic sealing member 21 protruded to the outside beyond the cylindrical portion of the electrode. The measurements were conducted in the same manner as described above. The measurement results are presented in Table 2.

[0039]

[Table 2]

Total number of batteries used for measurements : 20

E1/F or E2/F (%)	Discharge capacity via 10 Ohm load (mAh)	Occurrence of leakage after 100 h (number of batteries; the discharge end voltage is 0.9 V)
1.0	1642	12
1.5	1921	8
2.0	2078	3
2.5	2425	0
3.0	2415	0
5.0	2416	0
7.5	2390	0
10.0	2394	0
15.0	2386	0
20.0	2387	0
25.0	1982	0
30.0	1837	0

[0040] Data presented in Table 2 show that when the E1/F, E2/F ratios are less than 2.0%, the resistance to leakage decreases. When the E1/F, E2/F ratios are above 2.5%, the occurrence of leakage becomes zero and the leakage resistance characteristic of the batteries is good. However, when the E1/F, E2/F ratios exceed 25.0%, the reaction surface area and the amount of the negative electrode mix decrease and the discharge capacity drops. Therefore, it is preferred that the E1/F, E2/F ratios be within a range from no less than 2.5% to no more than 20.0%. Furthermore, it is necessary that this requirement be met for both ratios. Thus, when either of the E1/F and E2/F ratios did not meet this requirement, the effect was found to decrease.

[0041] Embodiment 4

An air - zinc battery 51 was fabricated in the same manner as in Embodiment 51, except that the projection processing was conducted, as shown by the ring-like groove G, after the peripheral portion of the electrode was inserted in the grooves made in the metallic sealing members 21, 22, as shown in Fig 5. Then the batteries of Embodiment 4 and the above-described batteries of Embodiment 1 and the conventional example (a total of 20 batteries of each type) were fully charged and discharged to an end voltage of 0.9 V. Then, the occurrence of leakage after 100 h and the occurrence of leakage after 500 h were studied. The results obtained are shown in Table 3.

[0042]

[Table 3]

	Occurrence of leakage after 100 h (number of batteries; the discharge end voltage is 0.9 V	Occurrence of leakage after 500 h (number of batteries; the discharge end voltage is 0.9 V
Embodiment 1	0	3
Embodiment 4	0	0
Conventional example	11	18

[0043] As follows from Table 3, the batteries of Embodiment 4 showed no leakage even after the utilization under more severe conditions, that is, after 500 h. Therefore, it is clear the projection processing conducted in the grooved structural parts of the metallic sealing members 21, 22 improves leakage resistance.

[0044]

[Effect of the Invention] As described above, with the cylindrical electrode in accordance with the present invention and an air – zinc battery employing such a cylindrical electrode, a battery can be obtained which has excellent resistance to leakage, discharge characteristic, and discharge capacity. Furthermore, since the collection of current onto the positive electrode case also serving as the positive electrode terminal is conducted via a metallic sealing member having a high strength, a battery can be provided which has a small spread of current collection characteristic.

[Brief Description of the Drawings]

Fig 1 shows an embodiment of the cylindrical electrode in accordance with the present invention. Fig (a) shows a partial cross section thereof, and Fig (b) is an exploded view of its main portion.

Fig 2 shows the structure of the air – zinc battery in accordance with the present invention.

Fig 3 shows another embodiment of the cylindrical electrode in accordance with the present invention.

Fig 4 shows another embodiment of the cylindrical electrode in accordance with the present invention.

Fig 5 shows another embodiment of the cylindrical electrode in accordance with the present invention.

Fig 6 shows the conventional cylindrical electrode. Fig (a) shows a partial cross section thereof, and Fig (b) is an exploded view of its main portion.

Fig 7 shows the structure of the conventional air – zinc battery.

[Legends]

1 – reaction layer; 2 – metallic collector; 3 – gas permeable membrane; 4 – air diffusion electrode; 5 – separator; 6 – negative electrode mix; 7 – negative electrode collector pin; 8, 10, 11 – gasket; 9 – lead wire; 12 – outer case; 13 – negative electrode terminal sheet; 14 – positive electrode terminal sheet; 15 – neck portion; 16 – air opening; 21, 22 – metallic sealing member; 23 – positive electrode case, 50, 60 – cylindrical electrodes; 51, 61 – air-zinc battery

Fig 1

1 – reaction layer; 2 – metallic collector; 3 – gas permeable membrane; 21 – metallic sealing member; 22 – metallic sealing member; 50 – cylindrical electrode

Fig 2

4 – air diffusion electrode; 5 – separator; 6 – negative electrode mix; 7 – negative electrode collector pin; 8 – gasket; 13 – negative electrode terminal sheet; 16 – air opening; 21 – metallic sealing member; 22 – metallic sealing member; 23 – positive electrode case, 50 – cylindrical electrode; 51 – air-zinc battery

Fig 3

Fig 4

Fig 5

G – projection processing

Fig 6

60- cylindrical electrode

Fig 7

4 – air diffusion electrode; 5 – separator; 6 – negative electrode mix; 7 – negative electrode collector pin; 8 – gasket; 9 – lead wire; 12 – outer case; 13 – negative electrode terminal sheet; 14 – positive electrode terminal sheet; 15 – neck portion; 16 – air opening; 60 – cylindrical electrodes; 61 – air-zinc battery

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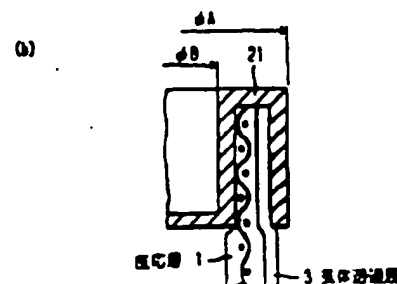
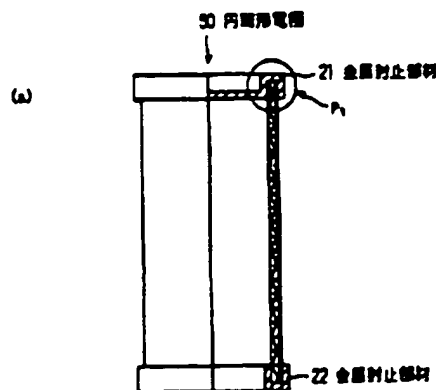
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(54) 【発明の名称】 円筒形電極およびこれを用いた空気亜鉛電池

(57) 【要約】

【課題】 機械的強度に優れた円筒形電極を構成すると共に、耐漏液特性、放電特性に優れ、また放電容量が大きく、且つ集電のバラツキの少ない円筒形の空気亜鉛電池を提供する。

【解決手段】 酸素還元能を有する反応層1と、金属集電体2と、親水性の気体透過膜3とから構成される中空円筒の電極と、環状の溝部を有する、円盤状の金属封止部材21と、環状の溝部を有する、環状の金属封止部材22とから構成され、前記電極の一方の開口端を前記円盤状の金属封止部材21の溝部に挿入して圧着し、また、前記電極の他方の開口端を前記環状の金属封止部材22の溝部に挿入して圧着して円筒形電極50を形成する。この円筒形電極50を用いて円筒形の空気亜鉛電池を構成する。



【特許請求の範囲】

【請求項1】 少なくとも、

酸素還元能を有する反応層と、金属集電体と、親水性の気体透過膜とから構成される中空円筒の電極と、
現状の溝部を有する、現状の金属封止部材と、
現状の溝部を有する、円盤状の金属封止部材とからなり、前記電極の一方の開口端を前記現状の金属封止部材の溝部に挿入して圧着し、前記電極の他方の開口端を前記円盤状の金属封止部材の溝部に挿入して圧着する構成であることを特徴とする円筒形電極。

【請求項2】 前記円盤状の金属封止部材の円盤中央部は、電極の円筒部より外部に突出した形状であることを特徴とする、請求項1に記載の円筒形電極。

【請求項3】 前記現状の金属封止部材の溝部の深さ、および前記円盤状の金属封止部材の溝部の深さは、電極の円筒部の長さに対して2.5%以上、20%以下であることを特徴とする、請求項1に記載の円筒形電極。

【請求項4】 前記現状の金属封止部材、および前記円盤状の金属封止部材は金属板から加工形成されていることを特徴とする、請求項1に記載の円筒形電極。

【請求項5】 前記現状の金属封止部材、および前記円盤状の金属封止部材の溝部外壁は、電極の開口端が挿入された後、現状のプロジェクション加工が施されていることを特徴とする、請求項1に記載の円筒形電極。

【請求項6】 請求項1に記載の円筒形電極の、円盤状の金属封止部材により密封された側を、正極端子を兼ねる有底円筒状の正極ケースの底側に向けて挿入して密着させ、正極側の集電を行うことを特徴とする空気亜鉛電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は耐漏液特性、放電特性に優れた円筒形電極と、これを用いた空気亜鉛電池に関する。

【0002】

【従来の技術】近年の携帯形電子機器の発達に伴い、その電源である電池に対して、より大きな電流が取り出せ、且つ長時間の使用が可能であることの要望がますます高まってきている。さらに最近では地球環境の保護や資源の有効利用に大きな関心が集まっており、これらの要望に対しても答えることが社会的要請となってきた。

【0003】これらの要望に答える有力な電池系として、酸素を正極活物質として使用する燃料電池や空気亜鉛電池等が知られている。これらの電池系は他の電池系と比較して、正極活物質が酸素であるため環境に対する影響が小さく、さらに取り出される電気容量の点でも優れている。特に空気亜鉛電池は体積当たりのエネルギー密度が優れているため、将来の携帯用電源として大きな

【0004】ところで、空気亜鉛電池はボタン形状、コイン形状の小型のものが補聴器用、ページャー用等の電源として流通しているのが現状である。しかしながら、これらの小形電池では用途が限定されるため、より広範囲な用途に対応可能な円筒形の空気亜鉛電池が望まれているところである。

【0005】さて、この空気亜鉛電池は正極活物質として酸素を、負極活物質として亜鉛を使用し、さらに電解液として強アルカリ水溶液を用いる。従って、この型の電池は電解液の漏出に対して十分な防止対策がとられていなければならない。

【0006】つきに従来より提案されている円筒形の空気亜鉛電池について図6および図7を参照して説明する。ここで図6は従来より提案されている円筒形電極の構造であって、同図(a)はその一部断面を示す図であり、同図(b)は(a)のP2で示す部位の拡大図である。また、図7は従来より提案されている円筒形の空気亜鉛電池の構造を示す図である。

【0007】従来の円筒形電極60は図6(a)に示すように中空円筒状であって、同図(b)に示すように酸素還元能を有する反応層1と、金属集電体2と、親水性の気体透過膜3から構成されている。

【0008】この円筒形電極60を用いた空気亜鉛電池61の構造は図7に示すように、円筒形電極60がその正極であって、この円筒形電極60の正極端子側の開口端は、ガスケット10、正極端子板14、ガスケット11の所定の位置に配設され、また、金属集電体2と正極端子板14はリード線9を介して電気的接続をとっている。また、気体透過膜3の外側には空気拡散層4が設けられ、反応層1の内壁には不織布等からなる有底円筒状のセパレータ5が、その底部を正極端子板14側にして装着されている。このセパレータ5の内部に粒状亜鉛、水酸化カリウム水溶液、増粘材等からなるゲル状の負極合剤6が配設されている。

【0009】また、円筒形電極60の負極端子側の開口端は、ガスケット8が所定の位置に配設され、さらに負極端子板13を配置してから空気孔16を有する外装缶12を被せ、絞り加工によるくびれ部15と外装缶12の開口部を内側に屈曲させることによって電池内部の構成部材を封入している。尚、負極の集電は負極合剤6中に挿入される釘状の負極集電ピン7と負極端子板13とを電気的に接続して行われる。また、空気電池は使用時まで空気孔16を塞いでおく必要があるが、このためのシール部材の図示は省略している。

【0010】しかしながら上述した構成の円筒形電極60では、反応層1、金属集電体2、気体透過膜3の3つの構成部材の機械的強度が低いことため外的な応力に対して極めて弱い。従って、開口端を負極端子板13側のガスケット8へ埋設することと、外装缶12にくびれ部15

圧縮とによるだけでは強固な封口状態が得にくい欠点を有していた。このため電池の放電が進行して負極合剤6の体積が膨張するに伴い、電池の内圧が上昇して正極の固定部位からの電解液漏出が認められることがあった。また、電解液の漏出に伴い電池内部の電解液が不足し、電池の放電持続時間を低下させるという欠点があった。

【0011】さらに、リード線9を用いた正極の集電は、そのリード線9の接続が技術的に難しく、また、接続部の接触抵抗のバラツキが大きいため、放電特性が一定にならず、不良の発生が起りやすいものであった。尚、放電の進行により電池の内圧が上昇する理由は、負極の亜鉛粉が電池の放電反応に伴って酸化亜鉛に変化し、負極中の固形成分の体積が膨張するためである。

【0012】また、上述した円筒形の空気亜鉛電池の課題に対して、米国特許第5,518,834等々に示されているように、円筒形電極の開口端を封止する部材を一部金属製にするなどして改良が試みられているが、十分な信頼性が得られるに至っていないのが実情である。

【0013】

【発明が解決しようとする課題】従って本発明の課題は、外的応力が加わっても変形等が生じない機械的強度に優れた円筒形電極を構成すると共に、耐漏液特性、放電特性に優れ、また放電容量が大きく、且つ正極の集電の信頼性が高く、集電のバラツキの少ない円筒形の空気亜鉛電池を提供する。

【0014】

【課題を解決するための手段】本発明は上記課題に鑑み成されたものであり、請求項1に記載の発明は、少なくとも、酸素還元能を有する反応層と、金属集電体と、親水性の気体透過膜とから構成される中空円筒の電極と、環状の溝部を有する、環状の金属封止部材と、環状の溝部を有する、円盤状の金属封止部材とからなり、前記電極の一方の開口端を前記環状の金属封止部材の溝部に挿入して圧着し、前記電極の他方の開口端を前記円盤状の金属封止部材の溝部に挿入して圧着する構成の円筒形電極を形成する。

【0015】また、請求項2に記載の発明は、前記円盤状の金属封止部材の円盤中央部を電極の円筒部より外部に突出した形状とする。

【0016】また、請求項3に記載の発明は、前記環状の金属封止部材の溝部の深さ、および前記円盤状の金属封止部材の溝部の深さを、電極の円筒部の長さに対して2.5%以上、20%以下の範囲に形成する。

【0017】また、請求項4に記載の発明は、前記環状の金属封止部材、および前記円盤状の金属封止部材は金属板から加工形成する。

【0018】また、請求項5に記載の発明は、前記環状の金属封止部材、および前記円盤状の金属封止部材の溝部外壁を、電極の開口端が挿入された後、環状のプロジ

【0019】さらに、請求項6に記載の発明は、請求項1ないし請求項5に記載の円筒形電極の、円盤状の金属封止部材により密封された側を、正極端子を兼ねる有底円筒状の正極ケースの底側に向けて挿入して密着させ、正極側の集電を行う円筒形の空気亜鉛電池を構成して上記課題を解決する。

【0020】請求項1に記載の発明によると、円筒形電極の両端の開口端を、この開口端を挟み込む溝構造を有する円盤状の金属封止部材と環状の金属封止部材により強固に固定するので金属集電体と金属封止部材とが圧接して、安定した電氣的接続が得られ、集電のバラツキが低減すると共に、反応層と気体透過膜とも圧縮されてとめられるため電極の機械的強度が向上することになり、外的応力に対しても変形等が生じることはなく、従って電解液の密封状態を確保することができて耐漏液特性が向上する。

【0021】また、請求項2に記載の発明によると、円盤状の金属封止部材の中央部を円筒形電極の外側に突出させることにより、放電容量の向上を図ることができる。

【0022】また、請求項3に記載の発明によると、円盤状の金属封止部材および環状の金属封止部材の、円筒形電極の開口部を挿入する溝部の深さを最適化することにより、さらなる耐漏液性の向上と、放電容量の向上を図ることができる。

【0023】また、請求項4に記載の発明によると、円盤状の金属封止部材および環状の金属封止部材を板状の金属材料からしほり加工等によって形成するので、生産性とコストに優れる。

【0024】また、請求項5に記載の発明によると、円盤状の金属封止部材および環状の金属封止部材の溝部外壁を、電極の開口端を挿入した後、環状のプロジェクション加工を施すので、耐漏液特性と集電特性がさらに向上する。

【0025】また、請求項6に記載の発明によると、電池の内部抵抗の抑制と抵抗値のバラツキが低減し、放電特性に優れ、且つ耐漏液特性に優れた円筒形の空気亜鉛電池を提供することができる。

【0026】

【発明の実施の形態】本発明の実施の形態について図1ないし図5を参照して説明する。図1は本発明にかかわる円筒形電極の実施例であって、同図(a)はその一部断面図であり、同図(b)は(a)のP1で示す部位の拡大図である。また、図2は図1に示す円筒形電極を用いた空気亜鉛電池の構造を示す図である。さらに、図3～図5は本発明にかかわる円筒形電極の他の実施例である。

【0027】実施例1

まず、円筒形電極について図1を参照して説明する。酸

ブラック、さらに固形分60%のポリテトラフルオロエチレンの水性分散液を各々の固形比で20:50:30になるように混合し、ペースト状の反応層混合物を得た。この反応層混合物を、表面にニッケルメッキを施した中空の円筒形ステンレスネットの金属集電体2に塗着し、これを乾燥後プレスロール工程を経て、厚さが0.8mmの円筒形の反応層1を作製した。その後、反応層1を親水機能を有する厚さ0.1mmの円筒状の気体透過膜3に挿入し、プレスロール工程を用いて、気体透過膜3と反応層1とを密着させ円筒形の電極を作製した。

【0028】つぎに、上述したようにして作製された円筒形の電極の両開口端に、この開口端を挟み込む溝部を有する金属封止部材21、22を装着し、全円周方向に沿って径方向に圧縮して円筒形電極50を構成する。このとき開口端部分での金属集電体2と金属封止部材21、22とが圧接され、電気的接続が得られる。また同時に反応層1と気体透過膜3も共に径方向に圧縮され強度が増大する。このとき金属封止部材21は円盤状であり、金属封止部材22は環状である。

【0029】また、このときの圧縮手段は、図1(b)に示す外径φAを小さくする方法、または内径φBを大きくする方法、またはその両方の方法で行うことが可能である。尚、金属封止部材21、22の材質にはスチールまたはSUSにNiメッキを施したもの、銅、黄銅等が用いられる。さらに、銅、黄銅の場合には錫メッキを施した物が好ましい。

【0030】上述したように作製された円筒形電極50を用いた空気亜鉛電池51の構成は図2に示すように、円筒形電極50の気体透過膜3の外側に不織布等からなる空気拡散層4を装着し、これを正極端子を兼ねる正極ケース23に挿入する。また、正極端子を兼ねる正極ケース23は側面に空気を取り入れる空気孔16を有している。つぎに、円筒形電極50の内面に沿って環状の金属封止部材22側の開口部から天然パルプ材の不織布よりなる有底円筒状のセパレータ5を、反応層1に当接するように挿入し、さらにこのセパレータ5の内側に粒状亜鉛、水酸化カリウム水溶液、増粘材等からなるゲル状の負極合剤6を充填する。

【0031】つぎに、ガスケット8を正極ケース23の開口部に挿入する。ガスケット8は金属封止部材22の内側と負極合剤6との接触防止を目的とする。これは負極合剤6中の粒状亜鉛は金属封止部材22と接触すると局部電池を構成し、負極活性物質である亜鉛の放電容量が低下するためである。また、ガスケット8の中央には釘状の負極集電ピン7が貫通され、負極合剤6に達している。

【0032】つぎに、正極ケース23の開口部を機械的に内側に屈曲させてカシメ封口し、外径が14mm、高さが50mmの円筒形の空気亜鉛電池51を作製した。

極50の集電は、円筒形電極50に装着されている金属封止部材21、22とが正極ケース23の内面に強く圧接されて確保される。即ち、円筒形電極50の金属集電体2は金属封止部材21、22を介して正極ケース23に低接触抵抗で接続される。一方、負極の集電は釘状の負極集電ピン7がガスケット8の中央部に圧入され、ガスケット8を貫通して負極合剤6に達し、他方は負極端子板13に接続することで確保される。

【0033】上述した方法により作製された空気亜鉛電池51と、従来例において示した空気亜鉛電池61とを同一サイズで作製し、つぎに示す特性の測定を行った。

(1) 放電容量: 10Ω負荷、終止電圧0.9Vにおける放電容量

(2) 漏液: 10Ω負荷、終止電圧0.9Vまで放電させた後、100時間経過後における漏液発生個数
その結果を表1に示す。

【0034】

【表1】

測定総個数20

	10Ω負荷 放電容量 (mAh)	放電終止電圧0.9V 100h経過後の 漏液発生数(個)
実施例1	2425	0
実施例2	2558	0
従来例	1952	11

【0035】表1から分かるように、実施例1の空気亜鉛電池51は従来より提案されている構造の空気亜鉛電池61に比して放電容量が増大し、また、放電後の漏液発生も認められない。

【0036】実施例2

図3に示すように円盤状の金属封止部材21の中央部を電極の円筒部よりも外部に突出させたこと以外は実施例1と同様にして空気亜鉛電池51を作製し、同様の測定を行った。測定結果を前掲の表1に示す。尚、図3に示す金属封止部材21の突出部と金属封止部材22の電極挟み込み部間の長さCは、金属封止部材21、22の電極挟み込み部間の長さDより長いことが望ましい。

【0037】表1から分かるように、実施例2の空気亜鉛電池51は実施例1よりも放電容量が増大し、また、放電後の漏液発生も認められない。

【0038】実施例3

図4に示すように、電極の周辺部を挿入する金属封止部材21、22の溝部の深さをそれぞれE₁、E₂とし、電極の長さをFとした場合、このE₁、E₂をFに対して1.0%~30%の範囲で変化させたこと(この場合、E₁=E₂とした)、および金属封止部材21の中央部を電極の円筒部よりも外部に突出させたこと以外は実施例1と同様にして空気亜鉛電池51を作製し、同様

【0039】

【表2】

測定総回数20

E ₁ /F又は E ₂ /F (%)	10Ω負荷 放電容量 (mAh)	放電終止電圧0.9V 100h経過後の 漏液発生数(個)
1.0	1642	12
1.5	1821	8
2.0	2078	3
2.5	2425	0
3.0	2415	0
5.0	2416	0
7.5	2390	0
10.0	2394	0
15.0	2386	0
20.0	2387	0
25.0	1982	0
30.0	1837	0

* 【0040】表2から分かるように、E₁/F、E₂/Fが2.0%以下になると耐漏液特性が低下する。E₁/F、E₂/Fが2.5%以上では漏液の発生は零であり、耐漏液特性に効果がある。一方、E₁/F、E₂/Fが25.0%以上では反応面積、および、負極量が減少し放電容量が低下する。従って、E₁/F、E₂/Fが2.5%以上、20.0%以下が好ましい。また、この条件は共に満足することが必要である。即ち、E₁/F、E₂/Fの一方が上記の条件から外れていると効果は低減することが確認されている。

【0041】実施例4

図5に示すように、電極の周辺部を金属封止部材21、22の溝部に挿入後、環状の溝Gで示すようにプロジェクション加工を施したこと以外は実施例1と同様にして空気亜鉛電池51を作製した。この実施例4と前述の実施例1、および従来例の電池のそれぞれ20個について、満充電で終止電圧0.9Vまで放電させた後、100時間経過後の漏液発生数と、500時間経過後の漏液発生数を調べた。その結果を表3に示す。

20 【0042】

* 【表3】

測定総回数20

	放電終止電圧0.9V 100h経過後の 漏液発生数(個)	放電終止電圧0.9V 500h経過後の 漏液発生数(個)
実施例1	0	3
実施例4	0	0
従来例	11	18

【0043】表3から分かるように、実施例4の電池はより過酷な条件である500時間経過後においても漏液の発生は認められない。従って、金属封止部材21、22の溝構成部にプロジェクション加工を施すことにより耐漏液特性が向上することが分かる。

【0044】

【発明の効果】以上説明したように、本発明の円筒形電極、およびこの円筒形電極を用いた空気亜鉛電池によれば、耐漏液特性に優れ、且つ放電特性、放電容量に優れた電池が提供できる。また、正極端子を兼ねた正極ケースへの集電は強度の高い金属封止部材を介して行えるため、集電特性にバラツキの少ない電池が提供できる。

【図面の簡単な説明】

【図1】 本発明にかかわる円筒形電極の実施例であって、(a)はその一部断面を示す図であり、(b)はその要部拡大図である。

【図2】 本発明にかかわる空気亜鉛電池の構造を示す図である。

30※【図3】 本発明にかかわる円筒形電極の他の実施例である。

【図4】 本発明にかかわる円筒形電極の他の実施例である。

【図5】 本発明にかかわる円筒形電極の他の実施例である。

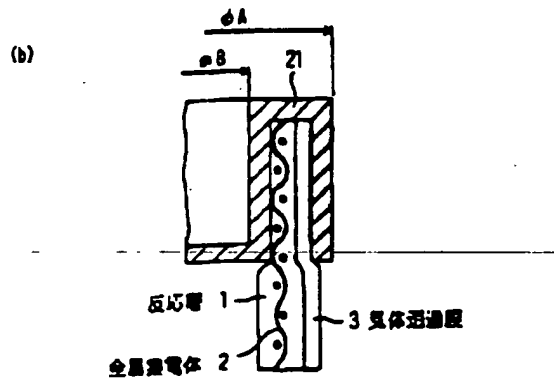
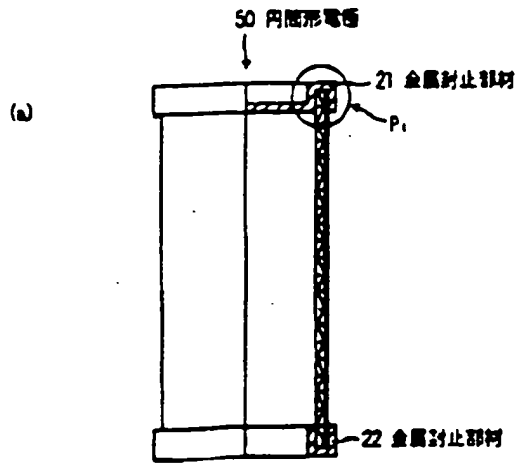
【図6】 従来の円筒形電極であって、(a)はその一部断面を示す図であり、(b)はその要部拡大図である。

【図7】 従来の空気亜鉛電池の構造を示す図である。

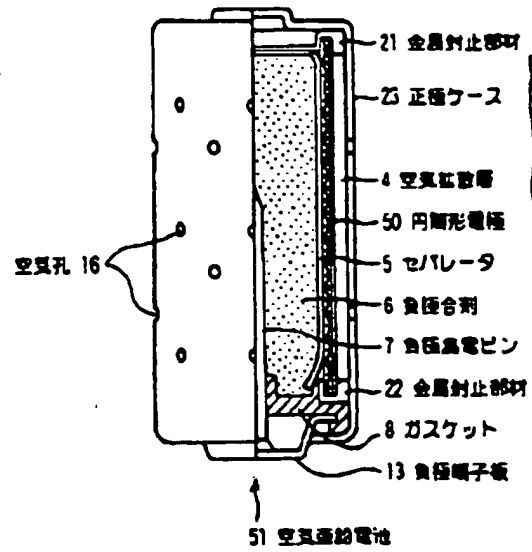
40 【符号の説明】

1…反応層、2…金属集電体、3…気体透過膜、4…空気拡散層、5…セパレータ、6…負極合剤、7…負極集電ピン、8、10、11…ガスケット、9…リード線、12…外装缶、13…負極端子板、14…正極端子板、15…くびれ部、16…空気孔、21、22…金属封止部材、23…正極ケース、50、60…円筒形電極、51、61…空気亜鉛電池

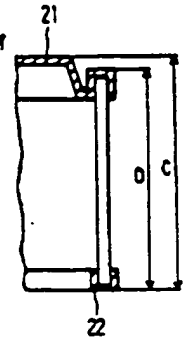
【図1】



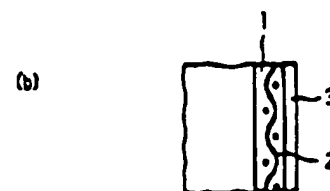
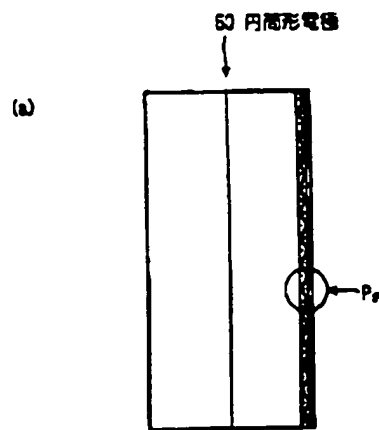
【図2】



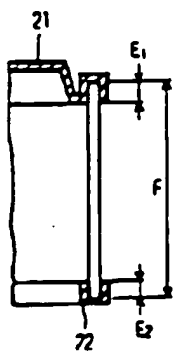
【図3】



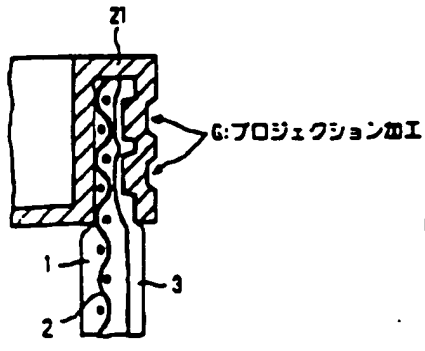
【図6】



【図4】



【図5】



【图7】

